ions. Mo^{II} and Re^{III}, which are the species formally present in the two cases, are isoelectronic (d^4). However, if each were to adopt the other's structure, we should have $[Mo_3Cl_{12}]^{6-}$ and $[Re_6Cl_8]^{10+}$. The charges in both cases are quite high, and, in the former case, there is the added consideration that even the $[Mo_3Cl_9]^{3-}$ core would have a substantial negative charge, so that it would be unlikely to combine with $3Cl^-$ to give $[Mo_3Cl_{12}]^{6-}$.

In summary, the combined requirements of filling only the bonding molecular orbitals and satisfying electrostatic requirements may place very severe restrictions on how many metal atom clusters are capable of existence. Nonetheless, chemical studies of the lower oxidation states of the heavier transition metals should be carried out with at least some alertness to the possibility of encountering further metal atom cluster compounds.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

Molecular and Electronic Structures of Some Thiourea Complexes of Cobalt(II)[1a]

BY F. A. COTTON,[1b] O. D. FAUT, AND J. T. MAGUE[1c]

Received July 26, 1963

Five thiourea (TU) complexes of cobalt(II) have been prepared and studied spectroscopically and magnetically. The results of spectroscopic and magnetic studies show that $Co(TU)_2Cl_2$, $Co(TU)_2Br_2$, $[Co(TU)_4](ClO_4)_2$, and $[Co(TU)_3SO_4]$ contain tetrahedrally coordinated sulfur. It is also shown that thiourea occupies a position comparable to various oxygen ligands near the low end of the spectrochemical series and that, like some other sulfur ligands, it causes an exceptionally large nephelauxetic effect ($\beta_{35} \leqslant 0.6$). $Co(TU)_4(NO_3)_2$ is shown to be an octahedral complex, though superficial interpretation of the reflectance spectrum might have suggested otherwise. Interpretation of the spectrum using an octahedral model necessitates the assumption of a very large nephelauxetic effect ($0.51 < \beta_{35} < 0.62$). This interpretation is substantiated by results for the similar complex $[Ni(thiourea)_6](NO_3)_2$ for which $\beta_{35} \approx 0.65$.

Introduction

Thiourea (TU) complexes of cobalt(II) were apparently first studied by Rosenheim and Meyer,[2] who reported $Co_2(TU)_7Cl_4$, $Co(TU)_4(NO_3)_2$, and $Co_2(TU)_3(SO_4)_2$. In a study of the phases of the $CoCl_2$–thiourea–water system at 35°, $Co_2(TU)_7Cl_4$ was reported again along with $Co(TU)_2Cl_2$.[3] Both compounds were reported to be blue. $Co_2(TU)_7Cl_4$ was stated to have a molar magnetic susceptibility of $17{,}420 \times 10^{-6}$ c.g.s. unit at 35° with a magnetic moment of 3.77 B.M. These two numbers are inconsistent, however; assuming the susceptibility to be correct, $\mu_{eff} = 4.66$ B.M. per cobalt atom. For $Co(TU)_2Cl_2$ the molar susceptibility was reported to be 6719×10^{-6} c.g.s. unit at 35°, giving a moment of 4.05 B.M. A moment of this magnitude is inconsistent with any of the three plausible assumptions for the coordination geometry, *viz.*, octahedral,[4] tetrahedral,[5] or planar.[6] The compounds $Co(TU)_2(NCS)_2$ and $Co(TU)_4Cl_2$ have been reported and their structures proved (by comparison with the known structures of isomorphous nickel complexes) by Nardelli, *et al.*[7–10] It has also been shown[8] that $Co_2(TU)_7Cl_4$ is actually $Co(TU)_4Cl_2$. When the appropriate correction is applied to the moment of 4.66 B.M. given above for $Co_2(TU)_7Cl_4$ it becomes 4.87 B.M., which is in good agreement with the value of μ_{eff} at room temperature obtained in this laboratory[11] previously, namely, 4.90 B.M.

From these fragmentary results, it appeared that a more detailed investigation of thiourea complexes, along lines previously followed for other cobalt(II) complexes,[5,12] would prove fruitful.

Experimental

Preparation of Compounds. $Co(thiourea)_4(NO_3)_2$.—$Co(NO_3)_2 \cdot 6H_2O$ (2.91 g., 0.01 mole) was dissolved in 25 ml. of hot butanol, 3.04 g. (0.04 mole) of thiourea was added, and the mixture heated to boiling, until all solid had dissolved, the solution changing from red to blue. On cooling, a blue solid separated. This was suction filtered, washed with ether, dried under vacuum, and then recrystallized from ethyl acetate. This produced large green-blue crystals which were ground and dried under vacuum at 100°; yield 4.4 g. The compound is soluble in hot ethyl acetate, acetone, and hot acetonitrile, giving purple solutions. It is decomposed by nitromethane and is insoluble in tetrahydrofuran, carbon disulfide, and methylene chloride.

---

[1] (a) Supported by the National Science Foundation; (b) Fellow of the Alfred P. Sloan Foundation; (c) N. S. F. Predoctoral Fellow.

[2] A. Rosenheim and V. J. Meyer, *Z. anorg. allgem. Chem.*, **49**, 13 (1906).

[3] S. K. Siddharta and K. Swaminathan, *Proc. Symp. Chem. Co-ord. Compounds, Agra, India*, **II**, 97 (1957).

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

[5] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

[6] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).

[7] M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. chim. ital.*, **87**, 917, (1957).

[8] M. Nardelli, L. Cavalca, and A. Braibanti, *ibid.*, **86**, 867 (1956).

[9] M. Nardelli, A. Braibanti, and G. Fava, *ibid.*, **87**, 1209 (1957).

[10] L. Cavalca, M. Nardelli, and A. Braibanti, *ibid.*, **86**, 942 (1956).

[11] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960)

[12] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

Table I

Analytical Data and Other Characteristic Properties of the Cobalt Thiourea Complexes

			Analyses[a]							
			Theory				Found			
Compound	Color	M.p., °C.	C	H	N	S	C	H	N	S
$Co(CH_4N_2S)_2Cl_2$	Blue	148	8.52	2.86	19.88	...	8.54	2.72	19.9	...
$Co(CH_4N_2S)_2Br_2$	Green-blue	163	6.48	2.17	15.14	...	6.92	2.21	15.0	...
$Co(CH_4N_2S)_4(NO_3)_2$	Green-blue	127	9.86	3.31	28.75	...	10.00	3.01	28.3	...
$Co(CH_4N_2S)_3SO_4$	Blue	~160 dec.	9.40	3.16	21.90	33.40	9.60	2.94	21.3	33.2
$Co(CH_4N_2S)_4(ClO_4)_2$	Blue-green	136–139	8.54	2.87	19.93	...	8.72	2.78	19.5	...

[a] Microanalyses by S. M. Nagy, M.I.T., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Table II

Magnetic Properties of Some Thiourea Complexes of Cobalt(II)

		Compound				
Run No.[a]	Property[b]	$Co(CH_4N_2S)_2Cl_2$	$Co(CH_4N_2S)_2Br_2$	$Co(CH_4N_2S)_3SO_4$	$Co(CH_4N_2S)_4(NO_3)_2$	$Co(CH_4N_2S)_4(ClO_4)_2$
1	μ	4.44	4.47	4.38	4.69	4.52
	θ	−11	−7	−4	−8	−7
2	μ	4.46	4.52	4.39	4.69	4.49
	θ	−13	−8	−4	−7	−11
3	μ		4.49		4.67	
	θ		−5		−8	
4	μ				4.81	
	θ				−18	
5	μ				4.75	
	θ				−19	

[a] Each run involves a fresh packing of the sample tube and the measurement of susceptibility at ~10 temperatures between about 78 and 300°K. [b] μ and θ are defined by the Curie–Weiss expression, $\mu = 2.83[\chi_{\rm Mol}^{\rm corr}(T - \theta)]^{1/2}$. In each run the values of μ and θ quoted give a curve from which $\chi_{\rm Mol}^{\rm corr}$ may be calculated to within the experimental uncertainty at any temperature in the range of the measurements.

$[Co(thiourea)_4](ClO_4)_2$.—$Co(ClO_4)_2\cdot 6H_2O$ (10 g., 0.028 mole) was dissolved in a minimum amount of hot isopropyl alcohol, and 0.86 g. (0.112 mole) of thiourea was added. The solution was allowed to cool and chloroform was added until the dark blue-green solution became slightly turbid. The solution was then placed in a refrigerator (~5°) for several days. The precipitate frequently appeared first as an oil which slowly crystallized. The solid was filtered and recrystallized from an isopropyl alcohol–chloroform mixture, affording dark blue-green plates.

$Co(thiourea)_3SO_4$.—$CoSO_4\cdot 7H_2O$ (2.81 g., 0.01 mole) was dissolved in 50 ml. of hot methanol, with caution against overheating since this sometimes produces an insoluble solid. Thiourea (3.04 g., 0.04 mole) was dissolved in 50 ml. of hot methanol and this was added to the first solution. The resulting deep blue solution was set aside to cool and after 24 hr. the solid which formed was suction filtered and dried at 100°; yield 2.9 g. The complex is insoluble in all common solvents tested, *viz.*, methanol, ethanol, benzene, ethyl acetate, acetonitrile, nitromethane, nitrobenzene, acetone, and tetrahydrofuran. It is decomposed by pyridine and 2-nitropropane. In one instance, the material which crystallized from the reaction mixture was green but it turned blue slowly on heating at about 85°, on treatment with hot nitromethane, or on standing for about 1 month. The significance of this color variation is not known.

$Co(thiourea)_2Cl_2$.—$CoCl_2\cdot 6H_2O$ (4.75 g., 0.02 mole) was dissolved in 30 ml. of hot *n*-butyl alcohol and 3.04 g. (0.04 mole) of thiourea added. The mixture was heated until all the solid dissolved. After this solution had cooled to room temperature, benzene was added until a slight, permanent turbidity was produced. On further cooling in an ice chest, a blue solid separated. This was suction filtered and dried at 60° under vacuum; yield 4.9 g. The molar conductance in nitromethane (0.001 *M*) was 3.1 ohm^{-1}. The complex is soluble in nitromethane, *t*-butyl alcohol, acetic anhydride, ethyl acetate, *n*-propyl alcohol, tetrahydrofuran, and hot acetic acid.

$Co(thiourea)_2Br_2$.—This was prepared in the same way as the dichloride using 3.26 g. of $CoBr_2\cdot 6H_2O$ and 1.52 g. of thiourea; yield 3.2 g.

$Co(thiourea)_2I_2$.—Neither the above method nor several others produced a pure sample of this compound. The oils or oily solids obtained were not characterized.

$Ni(thiourea)_6(NO_3)_2$.—$Ni(NO_3)_2\cdot 6H_2O$ (14.54 g., 0.05 mole) was dissolved in a minimum amount (~25 ml.) of nearly boiling isopropyl alcohol, and 15.22 g. (0.2 mole) of thiourea was added. A powdery, yellow-green precipitate of the product, contaminated with thiourea, formed immediately. This was separated from the cooled reaction mixture by filtration and recrystallized from hot acetone, giving 9.8 g. of yellow-green crystals, m.p. 168 dec.

Anal. Calcd. for $NiC_6H_{24}N_{14}O_6S_6$: C, 11.27; H, 3.79; N, 30.67. Found: C, 11.4; H, 4.07; N, 30.7.

The magnetic susceptibility of the solid measured at 300°, corrected for diamagnetism (-315×10^{-6}) and temperature-independent paramagnetism (243×10^{-6}), was 3900×10^{-6} c.g.s. unit, from which an effective magnetic moment at this temperature of 3.09 B.M. was calculated. The molar conductance of a 0.001 *M* solution in acetone was 221 ohm^{-1} mole^{-1}, which shows that the compound is an electrolyte.

Physical Measurements.—Infrared spectra, visible spectra, and magnetic measurements were made by methods previously described.[5,12] Each magnetic susceptibility run designated in Table II includes about ten measurements at about equal temperature intervals between 78 and 300°K. In all cases the points could be fitted within the estimated experimental uncertainties by a Curie–Weiss equation, $\mu = 2.84[\chi_{\rm Mol}^{\rm corr}(T - \theta)]^{1/2}$, using the values of μ (B.M.) and θ (°K.) recorded in Table II.

Discussion

The compounds prepared and studied are listed in Table I, which gives their colors, melting points, and analytical data.

In all cases, the infrared spectra indicate that the thiourea molecules are coordinated through the sulfur atoms only[13] according to the previous analysis by Yamaguchi, *et al.*[14]

---

(13) A tabulation of band positions and their interpretation is given in the Ph.D. thesis (M.I.T., 1962) of O. D. Faut. Essentially the same results and conclusions for the $Co(thiourea)_2X_2$ compounds are given in the thesis of Sr. Michael Schafer, S.P. (Notre Dame University, 1963); private communication from Br. Columba Curran.

(14) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

Chloro and Bromo Complexes.—For these, the interpretation of physical properties in terms of molecular structure is routine.[5,12,15] The very low molar conductance of the chloride in nitromethane confirms the expectation that the compound is a neutral molecule, undissociated in solution. The visible and near-infrared spectra are of the sort usually found in tetrahedral Co(II) complexes. Following usual procedures, these spectra were interpreted to give the parameters ν_2, ν_3, Δ, B', $f(\nu_2)$, and $f(\nu_3)$ as recorded in Table IV. From the magnetic moments and the Δ values, the λ' values, also recorded in Table IV, were obtained. All of these quantities are in the usual ranges for common tetrahedral Co(II) complexes.

$Co(thiourea)_4(ClO_4)_2$.—From the results recorded in Tables II, III, and IV for this compound, it may be concluded that it contains the tetrahedral $[Co(TU)_4]^{2+}$ ion, as might have been expected. Attention may be drawn to several interesting aspects of the behavior of this compound. First, the electronic spectrum is rather sensitive to the medium in which the $[Co(TU)_4]^{2+}$ is examined. Clearly, in acetone the complex cation tends to be solvolyzed or otherwise decomposed, but this can be prevented by addition of excess thiourea. It may be seen from Fig. 1 that when the concentration of excess thiourea reaches 0.05–0.10 M, a limiting spectrum is reached. We take this to be the spectrum of $[Co(TU)_4]^{2+}$. The spectrum of solid $[Co(TU)_4](ClO_4)_2$ is very similar in the visible except for the greater breadth of the absorption. The near-infrared band, however, is displaced ~1500 cm.$^{-1}$ to higher energies. Differences of this sort are occasionally observed[16] but are not common. The reason for the present one is unknown.

It may be noted that the B' value for Co(II) in $[Co(TU)_4]^{2+}$ is extremely low, 600 cm.$^{-1}$. In fact it is the smallest B' value so far reported for tetrahedral Co(II). According to a correlation previously suggested[17] this very low B' value should be coupled with very high band intensities and this is observed. The exceptionally large nephelauxetic effect caused by thiourea will be discussed further in connection with $Co(TU)_4(NO_3)_2$ below.

Using the Δ values[5] for $[CoCl_4]^{2-}$ and $[CoBr_4]^{2-}$ together with that for $[Co(TU)_4]^{2+}$, and adopting the average ligand field approximation,[5] one can estimate Δ values for $Co(TU)_2Cl_2$ and $Co(TU)_2Br_2$ of 3680 and 3580 cm.$^{-1}$, respectively. These are each ~200 cm.$^{-1}$ greater than the observed values, but since there is an uncertainty of ~100 cm.$^{-1}$ to be attached to any individual Δ value, these differences occasion no alarm. It is perhaps worth noting, however, that the direction of the discrepancies is the same as in previously reported comparisons of the same type.[5]

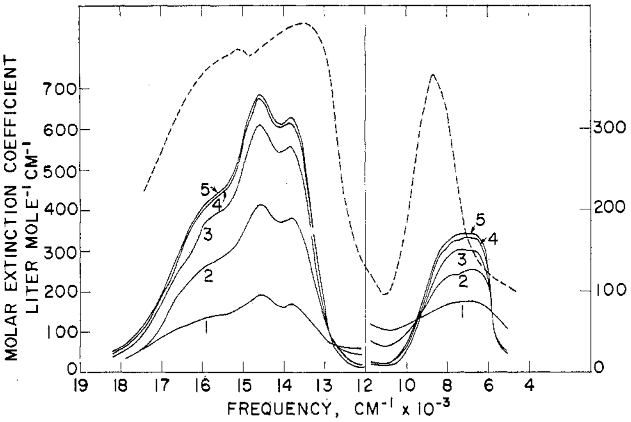

Fig. 1.—The visible and near-infrared spectrum of $[Co(TU)_4](ClO_4)_2$. Numbered solid curves show the spectra of a 1.00×10^{-3} M acetone solution containing the following molar concentrations of added thiourea: 1, 0.0; 2, 3.2×10^{-3}; 3, 8.0×10^{-3}; 4, 0.050; 5, 0.10. The dashed curve is the spectrum of the solid mulled in hexachlorobutadiene plotted with an arbitrary absorbance scale.

TABLE III

VISIBLE ABSORPTION SPECTRA

Compound	Band positions, cm.$^{-1}$ (ϵ)[a]	
	ν_3	ν_2
$Co(TU)_4(ClO_4)_2$[b]	15,600 sh	7,220 (172)
	14,580 (690)	
	13,890 (632)	
$Co(TU)_2Cl_2$[b]	16,200 (450)	7,350 (62)
	15,000 (490)	6,200 (81)
	13,800 (435)	5,500 (100)
$Co(TU)_2Br_2$[b]	15,600 (510)	7,350 (66)
	14,600 (600)	6,150 (76)
	13,900 (570)	5,300 (83)
$Co(TU)_3SO_4$[c]	16,700	~6,900
	15,400	
	14,100	
$Co(TU)_4(NO_3)_2$[d]	16,000	8,600
	14,500	
	13,700	

[a] Decadic molar extinction coefficient at peak. [b] Acetone solutions; 0.001 M for ν_3, 0.005 M for ν_2. [c] Diffuse reflectance spectrum of powdered solid. [d] Spectrum of solid mulled in hexachlorobutadiene.

$[Co(thiourea)_3SO_4]$.—The magnetic and spectroscopic data for this compound are strongly indicative of tetrahedral coordination of the cobalt ion, leading to the proposal of zwitterionic molecules, $[Co(TU)_3OSO_3]$. Excellent confirmation of this is obtained from the infrared spectrum. Coordination of a sulfate ion through one oxygen atom reduces the effective symmetry of the sulfate ion to C_{3v} and would be expected, *inter alia*, to (a) permit a mode similar in form to the totally symmetric S–O stretching mode of SO_4^{2-} to gain some intensity in the infrared and (b) split the triply degenerate S–O stretching mode of SO_4^{2-} into two infrared-active modes of A and E types. Exactly such effects have been observed by Nakamoto, *et al.*,[18] in $[Co(NH_3)_5OSO_3]^+$, where SO bands were found at 970 (m), 1130 (s), and 1038 (s). We find bands at 935 (m), 1150 (s), and 1026 (s), which can be attributed to coordinated sulfate and assigned analogously.

---

(15) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

(16) C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1963).

(17) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).

(18) K. Nakamoto, *et al.*, *ibid.*, **79**, 4904 (1957).

TABLE IV

ELECTRONIC STRUCTURE PARAMETERS FOR TETRAHEDRAL COBALT(II) COMPLEXES OF THIOUREA

Parameter	$[Co(CH_4N_2S)_4]^{2+}$	$Co(CH_4N_2S)_2Cl_2$	$Co(CH_4N_2S)_2Br_2$	$[Co(CH_4N_2S)_3SO_4]$
ν_2, cm.$^{-1}$	7,200	6,000	5,900	6,900
ν_3, cm.$^{-1}$	14,500	15,000	14,700	15,400
$f(\nu_2) \times 10^3$	2.98	1.33	1.16	...
$f(\nu_3) \times 10^3$	11.1	7.76	8.78	...
Δ, cm.$^{-1}$	4,250	3,480	3,390	4,000
B', cm.$^{-1}$	600	709	695	685
ΔB, cm.$^{-1}$ $(\beta)^a$	367 (0.62)	258 (0.73)	272 (0.72)	282 (0.71)
μ, B.M.	4.50	4.45	4.49	4.38
$-\lambda'$, cm.$^{-1}$	166	125	130	126

[a] Taking B for the gaseous Co^{2+} ion as 976, $\Delta B = 976 - B'$ and $\beta = B'/976$.

TABLE V

INFRARED BANDS RELEVANT TO THE STATE OF THE NITRATE ION IN $Co(TU)_4(NO_3)_2$ AND $[Ni(TU)_6](NO_3)_2$

Observed bands,[a] cm.$^{-1}$		Accepted ranges,[b] cm.$^{-1}$	
$Co(TU)_4(NO_3)_2$	$[Ni(TU)_6](NO_3)_2$	Ionic NO_3^-	$-ONO_2$
700–725 (w, ?)	710–740 (?)	690–720	
~760 (m, b)			780–820
821 (s, sp)	830 (w, sp)	822–831	
1049 (m, sp)		~1049	970–1034
1300–1350 (vb)	~1340 (?)		1250–1290
	1400 (s, b)	1400	
~1500 (?)	1500 (?)		1480–1530

[a] s, strong; m, medium; w, weak; v, very; b, broad; sp, sharp; ? indicates that assignment to nitrate is uncertain. [b] From B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957); K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963; and E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

$Co(thiourea)_4(NO_3)_2$.—Deducing the stereochemistry of the cobalt atom in this compound from the various physical data requires weighing the evidence a little more carefully than is usually necessary. The electronic spectrum of the solid, shown in Fig. 2, is quite similar to that of solid $[Co(TU)_4](ClO_4)_2$. Although the compound is soluble in a number of organic solvents, in every case examined there were color changes indicative of reaction or solvolysis and solution spectra have, therefore, not been considered valid. The spectrum of the solid does not, of course, afford any information on band intensities. Thus, the electronic spectrum is quite consistent with the postulate of a tetrahedral $[Co(TU)_4]^{2+}$ ion. On the other hand, in comparison with some well-known octahedral Co(II) complexes, $Co(TU)_4(NO_3)_2$ has its visible absorption at appreciably lower energies. $[Co(H_2O)_6]^{2+}$, for example, has its visible absorption centered around 20,000,[19] and H_2O is not very far from the weak end of the spectrochemical series. The position of the near-infrared band is inconclusive. Thus, the electronic spectral data might be considered to favor the $[Co(TU)_4](NO_3)_2$ formulation, with the cation tetrahedral.

The magnetic data seem decidedly against this, however. The observed magnetic moment (~4.75 B.M.) does not at all correspond with that for $[Co(TU)_4]^{2+}$ (~4.50 B.M.); it is, on the contrary, quite consistent with the occurrence of an octahedral coordination group made up of four thiourea sulfur atoms and two nitrate oxygen atoms, $[Co(TU)_4(ONO_2)_2]$.

The infrared spectrum of $Co(TU)_4(NO_3)_2$ was examined for evidence as to whether the nitrate ions are coordinated or not. Table V shows the observed bands as well as those for $[Ni(TU)_6](NO_3)_2$ in which the nitrate ions are not coordinated, together with the expected absorptions for ionic and coordinated nitrate ions. A question mark is used to indicate uncertainty—or even outright doubt—whether a band can be attributed to nitrate, not to indicate any uncertainty as to its presence. In the 690–720 cm.$^{-1}$ region, the thiourea absorption masks any possible nitrate absorption. In $Co(TU)_4(NO_3)_2$ a broad, medium band at ~760 cm.$^{-1}$ may be one of the absorptions due to coordinated nitrate, shifted slightly out of the usual range (780–800 cm.$^{-1}$); the thiourea does not seem to be responsible for absorption here, judging by the spectra of all the other complexes. There is also a band at 821 cm.$^{-1}$ which also seems to require the same assignment, if the nitrate is coordinated, though it can as well be assigned to ionic nitrate, as is the 830 cm.$^{-1}$ band of $[Ni(TU)_6](NO_3)_2$. The medium band at 1049 cm.$^{-1}$ is also susceptible of assignment to either ionic or coordinated nitrate. For the latter, it is a little out of the previously observed range, but not excessively. For ionic nitrate, it has exactly the right frequency and its intensity could be attributed to the influence of low site symmetry in the crystal. For the nickel complex, this band, which is the infrared forbidden A_1' N–O stretching mode in the unperturbed nitrate ion, is not seen at all, indicating high effective site symmetry in that case. In $Co(TU)_4(NO_3)_2$, there appears to be more absorption from 1300 to 1350 cm.$^{-1}$ but less at ~1400 cm.$^{-1}$ than in the nickel complex. The two spectra are quite similar at ~1500 cm.$^{-1}$, each having a strong band, which may, however, be due entirely to thiourea. It should be clear that while $[Ni(TU)_6](NO_3)_2$ could probably be taken to contain ionic nitrate on the infrared evidence alone, the infrared data for $Co(TU)_4(NO_3)_2$ are thoroughly inconclusive.

We conclude, however, that the magnetic moment correctly indicates octahedral coordination and that the proper interpretation of the electronic spectrum requires recognizing that sulfur-bonded thiourea produces an exceptionally large nephelauxetic effect. According to the simplest crystal field treatment of the

---

(19) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

quartet levels of the Co(II) ion in an octahedral field, ignoring the $^4T_1(F)$–$^4T_1(P)$ interaction, the energies of the four quartet states are as follows: $^4T_1(P)$, $15B$; $^4A_2$, 1.2Δ; $^4T_2$, 0.2Δ; $^4T_1(F)$, -0.6Δ. If the absorption band in the near-infrared is assigned to the $^4T_1(F) \rightarrow {}^4T_2$ transition, we obtain $\Delta_0 = 10{,}700$ cm.$^{-1}$. Assuming then that the $^4T_1(F) \rightarrow {}^4T_1(P)$ transition has an energy of 14,000–15,500 cm.$^{-1}$, we calculate that B' is between 500 and 600 cm.$^{-1}$. The $^4T_1(F) \rightarrow {}^4A_2$ transition is then expected to have an energy of $\sim$19,000 cm.$^{-1}$. It has been frequently observed in other octahedral Co(II) complexes that the $^4T_1(F) \rightarrow {}^4A_2$ transition is very weak in comparison to the $^4T_1(F) \rightarrow {}^4T_1(P)$ transition.[20] If that is also true here, and theory suggests that it should be generally true,[20] then the assignment of an octahedral field and the parameters $\Delta_0 \approx 10{,}700$ cm.$^{-1}$ and $500 < B' < 600$ cm.$^{-1}$ satisfactorily accounts for the observations.

It remains only to consider whether these parameters are themselves reasonable. The Δ_0 value is provided by four thiourea molecules and two nitrate ions. By comparison of the Δ values available for tetrahedral Co(II) complexes[5] with that for $[Co(TU)_4]^{2+}$, we may infer that thiourea makes a contribution to Δ of 1.0–1.2 times that made by oxygen ligands. Thus the appearance of the $^4T_1(F) \rightarrow {}^4T_2$ transition at $\sim$8600 cm.$^{-1}$ in $[Co(TU)_4(NO_3)_2]$, while the same transition occurs at $\sim$8000 cm.$^{-1}$ in $[Co(H_2O)_6]^{2+}$, is entirely reasonable. The range for B' leads to a value[21] for β_{35} in the range 0.51–0.62. This agrees satisfactorily with the β value obtained for $[Co(TU)_4]^{2+}$ (which is also a β_{35} in Jørgensen's notation). As first pointed out by Schäffer[22] and more recently re-emphasized by Jørgensen,[21,23] ligands which coordinate through sulfur frequently cause very pronounced nephelauxetic effects. Our results on Co(II) complexes indicate that the sulfur atom in thiourea, for which we know of no previous data, is no exception. It could also be said that the observation of large nephelauxetic effects in these complexes independently demonstrates that the thiourea molecules are coordinated through sulfur, as has been inferred from the infrared spectra.

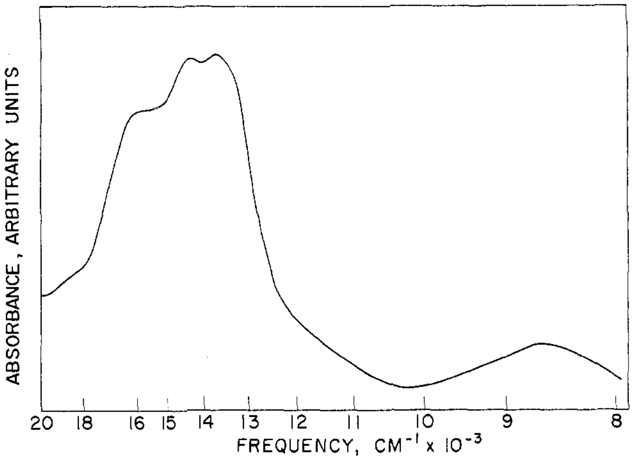

Fig. 2.—The visible and near-infrared spectrum of $Co(TU)_4(NO_3)_2$ recorded on a hexachlorobutadiene mull of the solid.

As a still further test of the structural assignment for $[Co(TU)_4(NO_3)_2]$ and in order also to test further the conclusion that thiourea produces an exceptionally large nephelauxetic effect when coordinated through sulfur, the compound $[Ni(TU)_6](NO_3)_2$ was prepared and studied. Although it was desired to prepare $[Ni(TU)_4(NO_3)_2]$ to afford a more direct comparison, this compound could not be obtained under the conditions employed. Since $[Ni(TU)_6](NO_3)_2$ is adequate for the purpose, no further efforts were made to prepare the direct analog to the cobalt compound.

The visible spectrum of $[Ni(TU)_6](NO_3)_2$ in acetone solution has bands at 22,200 (ϵ 62) and 13,800 cm.$^{-1}$ (ϵ 28) which may be assigned, respectively, to the $^3A_2 \rightarrow {}^3T_1(P)$ and $^2A_2 \rightarrow {}^3T_1(F)$ transitions. By solving the appropriate Tanabe and Sugano equations[24] one obtains $\Delta_0 = 8600$ cm.$^{-1}$ and $B' = 700$ cm.$^{-1}$. In excellent agreement with the results for the cobalt analog, Δ_0 is quite similar to that[20] in the hexaaquo ion (8500 cm.$^{-1}$), while B' is decreased very greatly from the free ion value (1080 cm.$^{-1}$). The decrement in B is about twice as great as any previously observed in octahedral nickel(II) complexes with more usual ligands,[25] giving $\beta_{35} = 0.65$.

---

[20] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962.

[21] C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1963). This article explains the meaning of β_{35}.

[22] C. E. Schäffer, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 24N.

[23] C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2017 (1962).

[24] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[25] Reference 21, Table VI.